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CONTROL MEASURES FOR *Cyanobacteria* AND *Cyanotoxins* IN DRINKING WATER

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Abstract

Algal bloom can represent a serious consequence of the eutrophication of surface water. Some of these algae, called cyanobacteria, are of particular interest for their effect on human health due to their capacity to produce cyanotoxins. In many countries, in fact, there are important problems of poisoning attributed to toxic cyanobacteria and contamination of water sources (specially lakes) resulting in increased cyanobacterial growth. *Cyanobacteria* can become particularly harmful for humans when water is used for drinking consumption; in fact, they can generate many problems in drinking water treatment plants (increase of solids load, bacterial growth in sand and GAC filters, low efficiency of disinfection) and in the distribution system (growth in reservoir tanks and pipes). Moreover, algal toxins produced by cyanobacteria can be released during water treatment and can persist in water until final consumption. For these reasons, appropriate technologies should be used for water treatment in order to efficiently remove cyanobacteria cells, to reduce the risk of cyanotoxins release and to efficiently remove dissolved toxins. In this work, an overview on the main conventional and advanced processes for *Cyanobacteria* and *Cyanotoxins* removal from drinking water will be presented. Moreover, the main results of an experimental research on the removal of *Cyanobacteria* cells (coagulation/flocculation, sand filtration, GAC filtration, chlorine oxidation) and of cyanotoxins (activated carbon) will be discussed.

Key words: Cyanobacteria, Cyanotoxin, drinking water, microcystin-LR

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1. Introduction

The use of lake water for drinking purpose can present some quality problems due to the presence of algae, turbidity, color and odorous compounds. *Cyanobacteria*, known as blue-green algae, are photosynthetic algae with dimension ranging from 1 µm to more than 100 µm.

They can be aggregated in colonies or filaments, and their growth and formation of blooms is influenced by a variety of physical and chemical factors like temperature, length of daylight, macronutrients (phosphorous and nitrogen) concentration, micronutrients (iron and molybdenum) concentration, alkalinity, pH and climatic conditions (Health Canada, 2002).

They are very common in lakes, artificial reservoirs, small natural reservoirs and rivers with weak flow; their proliferation is favored by the presence of light, high temperature, low turbulence, presence of nutrients. *Cyanobacteria* sanitary relevance is of concern for their capacity to produce algal toxins with toxic effects for human health.

Of the more than fifty known species, those most commonly associated with toxicity are *Microcystis*, *Planktothrix*, *Anabaena*, *Aphanizomenon*, *Nodularia*, *Schizotrix* capable of producing the following toxin classes:

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- Neurotoxins (toxic to the nervous system): *Anatoxin-a, Anatoxin-a (s), Homo-anatoxin-a, (Saxitoxin), Paralytic Shellfish Poisons*;
- Hepatotoxins (toxic to the liver): *Microcystina, Cylindrospermopsin*;
- Endotoxins (contact dermo-irritants): *Debromoaplysiatoxin, Lyngbyatoxin, Aplysiatoxin.*

The hepatotoxins (in particular the *Microcystin*) are the most frequent and can be released from the genera *Microcystis, Planktothrix, Anabaena, Aphanizomenon, Nodularia, Nostoc, Cylindrospermopsis* and *Umezakia*. Among the *Microcystins,* the most frequent and present in greater concentration is the *Microcystin-LR* (with toxic effect for humans), which is generally contained in the algal cell but can be easily released following cell lysis. *Microcystin-LR* is a potent inhibitor of eukaryotic protein serine/threonine phosphatases 1 and 2A; due to its toxic and carcinogenic effect for human health, a provisional guideline value of 0.001 mg/L (for total *Microcystin-LR,* free plus cell-bound) was indicate by WHO (WHO, 1999; WHO, 2006, WHO, 2011) and Funari et al. (2014).

Table 1 shows a correspondence between the cyanobacterial species and the toxins produced.

Table 1. Main cyanobacterial species and related toxins (WHO, 2004)

Cyanobacterial species	***Toxins***
Anabaena spp.	Anatoxin-a(S), anatoxin-a, microcystins, saxitoxins
Anabaenopsis millenii	Microcystins
Aphanizomenon spp.	Anatoxin-a, saxitoxins, cylindrospermopsin
Cylindrospermum spp.	Cylindrospermopsin, saxitoxins, anatoxin-a
Lyngbya spp.	Saxitoxins, lyngbyatoxins
Microcystis spp.	Microcystins, anatoxin-a (minor amount)
Nodularia spp.	Nodularins
Nostoc spp.	Microcystins
Oscillatoria spp.	Anatoxin-a, microcystins
Planktothrix spp.	Anatoxin-a, homoanatoxin-a, microcystins
Raphidiopsis curvata	Cylindrospermopsin
Umezakia natans	Cylindrospermopsin

Relevant concentrations of cyanotoxins in surface waters have been registered in many countries: China, Portugal, Australia, Finland, USA (WHO, 1999) and significant outbreaks in drinking water have been registered in Brazil, Zimbabwe, Cameroon, China, Austria and Australia (Health Canada, 2002). In Italy cyanobacterial blooms affect many regions and the main frequent genera are *Microcystis* (*M. aeruginosa* and *M. flos-aquae*), *Aphanizomenon* (*Ap. flos-aquae*) and *Anabaena* (*A. flos-aquae* and *A. planctonica*) and *Planktothrix rubescens* (Funari et al., 2006; Mattei et al., 2005).

In the most case, the cyanobacteria toxins naturally exist in intracellular form and are retained within the cells; so, when the cells die the toxins are released in water. This behavior can occur in the drinking water treatment plants after the application of some processes: in this case, the cyanobacteria toxins can increase.

The adoptable alternatives to reduce the risk of presence of cyanobacteria and cyanotoxins in water for human use are:

- an appropriate choice of source of supply, so as to avoid drinking water from contaminated sources;
- the reduction of nutrient supply (in particular phosphorus) to the source of supply;
- the use of adequate treatments for the removal of algae;
- the use of adequate treatments for the removal of algal toxins.

Below we will analyze the main treatments used in water treatment, paying particular attention to the effect they can have on the removal of cyanobacteria and cyanotoxins.

2. Technologies for cyanobacteria and cyanotoxins removal

Appropriate technologies for cyanobacteria control must reflect proper management of the watershed and reservoir to prevent algal growth, correct treatments for the removal of both cyanobacteria and their toxins and an appropriate monitoring program. In the following paragraphs, an overview on the treatment processes for their removal in drinking water treatment plants will be presented and discussed.

2.1. Pre-treatments

Micro sieving (mesh 20 - 40 μm) represents a valid technique for the physical separation of algal cells, with very variable yields depending on the cyanobacterial species (algal size), the cell aggregation (single cell, aggregates, filaments, etc.) and the presence of solids in water. Fine screens can cause cell lysis, and consequent release of toxins, which could occur because of cell rupture during filtration (WHO, 1999). Another effective pre-treatment is aeration, especially for the removal of volatile and gaseous compounds, such as carbon dioxide, hydrogen sulfide and volatile organic compounds associated with algal decomposition (WHO, 1999).

2.2. Chemical oxidation

Chemical oxidation is a widely used treatment in water purification and can be applied as pre-oxidation, intermediate oxidation or final disinfection. The specific effect may be that of cellular inactivation of algae with their subsequent immobilization in the flocs or inside the filters. Moreover, pre-oxidation can be considered one of the main methods of improving the subsequent coagulation and filtration processes, since it is able to reduce both the organic coating that

forms on colloidal particles and the stabilizing effect that algae can have on colloids and compromising their removal (Edzwald, 1993; Gibbs, 1983).

It is therefore evident that the practice of pre-oxidation (or oxidation along the treatment line) is a very controversial choice and must be carefully assessed based on the content of algal cells that can favor the formation of oxidation by-products and the release of cyanotoxins. Therefore, the application of oxidative treatments is optimal after having carried out a physical separation of algal cells and is mainly addressed to the removal of cyanotoxins.

The most commonly used oxidizing agents, based on their cost and the possibilities of their use, are chlorine or hypochlorite, chlorine dioxide, ozone, potassium permanganate. Tsuji et al. (1997) observed that microcystin-LR (MC-LR) removal after 60 minutes contact time was about 36% with a chlorine dose of 0.7 mg/L and 100% at a dose of 2.8 mg/L. Although these results seem to encourage the use of chlorine for toxin removal, pre-oxidation of the cells must be avoided, because it increases the risk of toxin release from algae and produce trihalomethanes during water treatment. Acero et al. (2005) found that chlorination could be applied in pre-oxidation and disinfection processes for cyanobacterial toxin control if the pH is kept below 8. Merel et al. (2010) found that chlorination is very effective on microcystins and its efficiency depends on pH, chlorine dose and oxidant nature.

As concerns chlorine dioxide, Kull et al. (2004) found that ClO_2 is not a suitable oxidant for the degradation of microcystins in drinking water treatment processes; moreover ClO_2 is rapidly consumed by fulvic and humic acids, leaving less ClO_2 residual to oxidise MC-LR and the generated oxidation products resulted to be nontoxic (Kull et al. 2006).

Montiel and Weltè (1998) have shown that ozone can represent a preliminary treatment able to improve the removal performance of algae from 75 to 95% with subsequent flotation treatments, rapid filtration on biolith or slow filtration on sand. The same conclusion was reached by Bauer et al. (1998) in the study of water treatment of the Thames, by analyzing the effects on multilayer pre-oxidation filtration with ozone and in-line filtration (dosing of coagulant inlet to filtration) with iron sulphate individually and combined: algae removal increased from about 50% without chemical additions to 90% with ozone and iron. Ozone pre-oxidation has proved particularly effective in the destruction of some classes of toxins, although many researchers agree that dosages and contact time depend on the quality of the water and the nature of the substance to be oxidized (Croll and Hart, 1996; Rositano, 1996).

A good removal of dissolved toxins was observed, with yields of 95% on MC-LR at a dose of 1 mg/L of potassium permanganate for 30–minutes contact time; however, the effect was decidedly negligible on intracellular toxins inside the algal cells, whose release, however, could be promoted during treatment (Lam et al., 1995). A kinetic database has been compiled by Rodrìguez et al. (2007a, b) for different oxidants and the results showed that permanganate can effectively oxidize *anatoxin-a* and MC-LR, while chlorine can oxidize *cylindrospermopsin* and MC-LR and ozone is capable of oxidizing all three toxins with the highest rate.

2.3. Coagulation/flocculation/sedimentation

The effectiveness of this treatment in algae removal is greatly influenced by the typical characteristics of algal cells such as the high motility and the elongated and filamentous geometry that can compromise the entrapment in the flakes. Bernhardt and Clasen (1991) have shown that there is a direct proportionality between the total surface area of the algae particle / cell, then the cell concentration, and the coagulant dosage required for the flocculation process, as long as the cell is more or less spherical and smooth. Hoeger et al. (2004) observed a removal of cyanobacteria cells of 99% with coagulation, flocculation and sedimentation. The removal with coagulation and flocculation of small and spherical algal cells is better than filamentous cells like *Planktotrix rubescens* (Bernhardt and Clasen, 1991). Coagulation/flocculation has a negligible effect on extracellular toxins removal. Rositano and Nicholson (1994) found no toxins removal by comparing ferric sulphate, alum and polyaluminium chloride.

The effectiveness of sedimentation is generally not satisfactory, not only because of the inevitable escape of the smaller flocs, but also because in the relatively long retention times of the water in the basin it is easier for the algae with greater motility to "free themselves" from the trap of the floc. However, as generally the algal flocs are very slow to settle, it is good to apply sedimentation with relatively low flow rates to facilitate the process (Edzwald, 1993). However, in the same basin, "new" algae can grow due to light and long retention time.

2.4. Dissolved air flotation

Although sedimentation is still the most widespread system for primary water clarification, flotation is indicated for the separation of naturally dense particles (such as algae). Hargesheimer and Watson (1996) confirm that flotation can obtain removals included in the range 29 - 85% against sedimentation that reaches a maximum of 49%. With floatation tests performed on waters rich in algae (>50,000 cells/L, 50% of which are blue-green algae), the removal percentages obtained are between 95% and 99%. Also, in the case of Dissolved Air Flotation (DAF), the efficiency of the treatment often depends on the type of algae, as well as on its concentration with removals between 57 and 100% (WHO, 1999).

2.5. Rapid sand filtration

Rapid sand filtration can remove up to 75% of cyanobacteria but its efficiency is very variable; if this

treatment is combined with a coagulation/flocculation or ozone oxidation, algae removal increases up to 90%. Algae with high motility (*Cryptomaonas, Rhodomonas,* etc.) are very resistant to filtration and the removal is generally lower than 50% (Petrusevski et al., 1995). Direct filtration seems to be more effective than rapid sand filtration (Bauer et al., 1998) on cyanobacteria removal. Otherwise, low sand filtration (hydraulic load of 0.5 - 1 m/h) is very efficient for cyanobacteria removal (WHO, 1999).

Some limits of the filtration treatment are the low yield of removal in the case of algae with high motility, the possibility of algal proliferation on the filtering support and the effect of cell lysis induced by the filter.

2.6. Activated carbon adsorption

Among the conventional processes, activated carbon adsorption, which is commonly adopted in drinking water treatment plants, appears to be one of the most effective option. The activated carbons derived from wood showed very interesting results, due to their high mesopore volume: Drikas (1994) showed that the use of 25 mg/L of wood-based PAC (with a contact time of 30 minutes) reduce the concentration of microcystin-LR from 50 μg/L to a value lower than 1 μg/L. MC-LR adsorption was improved with activated carbon with higher mesopore and macropore volume while Natural Organic Matter (NOM) caused a reduction in the capacity of carbon for MC-LR (Huang et al., 2007). Wang et al. (2009) observed that GAC filtration has shown to be promising as it is not only an efficient adsorbent, but also can support biodegradation of microcystins, extending the lifetime of this application. Up to 70% removal of microcystin-LR was still observed after 6 months of operation of the sterile GAC column, indicating that adsorption still played a vital role in the removal of this toxin.

The adsorption efficiency of the PAC for both MC-LR and MC-LA was affected by the amount of DOC in the water with lower adsorption for both compounds with higher DOC concentration (Cook and Newcombe, 2008). Pendleton et al. (2001) observed that both the adsorbent surface chemistry and the primary micropores volume have virtually no influence on the amount of MC-LR adsorbed and an adjustment of the solution pH conditions, to low pH, results in an enhanced adsorption of MC-LR. Craig and Bailey (1995) showed a significant breakthrough of MC after 5 months of operation of a GAC filter using an Empty Bed Contact Time (EBCT) of 15 minutes. In addition, they showed that an EBCT of 6 minutes resulted in a significant microcystin breakthrough after 1 month of operation. Moreover, Bernezeau (1994), using pilot scale tests on water with microcystins at 30-50 μg/L, showed microcystins removal higher than 90%, until 7,000-10,000 Bed Volumes (BV). After these values, the efficiency dropped to less than 63% due to the GAC saturation with dissolved organic carbon (DOC). The removal of MC-LR in a real treatment plant was evaluated by Lambert et al. (1996) that found that the conventional treatment processes combined with activated carbon generally removed more than 80% of MCs from raw water, with a residual concentration of 0.1 - 0.5 mg/L for both GAC and PAC treatment facilities. Sorlini and Collivignarelli (2011) observed a higher removal of MC-LR with mineral than vegetal activated carbon and limit concentration for MC-LR was reached after about 4,000 BV during column tests.

2.7. Combined treatments

The chemical oxidation processes are generally effective in cyanobacteria inactivation but they can cause toxin release due to the cells die and break open. The advantage is that algal cells, after inactivation, are immobilized and can be more easily removed by means flocculation or granular filtration. Among the chemical oxidation processes, ozonation is the most effective in cyanobacteria inactivation. Montiel e Weltè (1998) observed that ozone applied before flotation, rapid or slow sand filtration, increases algal cells removal from 75% to 95%. A treatment work including pre-oxidation, coagulation, flotation and filtration removes an average 96% of influent cells, while rapid gravity filters alone removes 63-75% (Henderson et al., 2008).

2.8. Advanced oxidation processes (AOPs)

AOPs are oxidation processes obtained by combining simultaneously different oxidants mainly H_2O_2, UV and O_3. Some researchers observed that H_2O_2 and UV radiation alone determine a negligible destruction of MC-LR (Tsuji et al., 1994). Similar results were observed studying the oxidation of MC-LR (10 mg/L) with variable-intensity UV radiation (up to 12 μE/(cm^2 s)) for a maximum exposure time of 60 minutes, showing no significant toxin reduction (Gajdek et al., 2004). Other researchers studied the effect of combining different UV radiation and H_2O_2 doses as well as different pH on MC-LR oxidation (0.15 mg/L). The authors found that H_2O_2 is ineffective, UV radiation ensures 85% oxidation yield after 90 minutes contact time (UV dose = 153 μW/cm^2 and pH = 7.2), while H_2O_2/UV process show a 95% oxidation yield after 32 minutes contact time (UV dose = 153 μW/cm^2, pH = 7.2 and H_2O_2 concentration of 2 mmol/L). Moreover, MC-LR degradation yields decrease with increasing pH (Li et al., 2009).

2.9. Membrane filtration

As concerns membrane processes, Chow et al. (1997) reported yields of removal of Microcystis aeruginosa over 98% by ultrafiltration with flat-sheet membranes. In the same study, experiments with different reverse osmosis membranes, however, showed removal yields for MC-LR of 96%. A study from Campinas and Rosa (2010) demonstrated that ultrafiltration with a hollow fiber cellulose acetate

membrane was an effective barrier against cyanobacteria, producing water free of M. aeruginosa and with a turbidity below 0.1 NTU, while it was ineffective against *Microcystin*.

The removal of intra and extra-cellular toxins by means of ultrafiltration and nanofiltration was studied by Gijsbertsen-Abrahamse et al. (2006). The ultrafiltration treatment was very effective in removing intracellular toxins, with a removal efficiency higher than 98%, while nanofiltration was effective in the removal of extracellular toxins, with a removal efficiency ranging between 96 and 99% depending on the type of toxin considered. Teixeira and Rosa (2006) confirmed the high removal efficiency of dissolved MC-LR and *anatoxin-a* by nanofiltration. Dixon et al. (2011) studied the removal of intra and extra-cellular cyanotoxins using a multi-barrier treatment consisting of coagulation, powdered activated carbon (PAC) adsorption and ultrafiltration. The system was able to reduce 90% of *saxitoxin* and 92% of intracellular *microcystin*. Other authors (Sorlini et al., 2013) observed that the removal rates of cyanobacteria and total algae content, with the use of microfiltration, are greater than 98% and between 98% and 99%, respectively.

2.10. Comparison among treatments

Treatment effective for the removal of cyanobacteria includes filtration to remove intact cells. Treatment effective against free *microcystins* in water (as well as most other free cyanotoxins) includes oxidation through ozone or chlorine at sufficient concentrations and contact times, as well as GAC and PAC applications (WHO, 2015). Table 2 reports an overview on the treatment performance for cyanobacterial cells and cyanotoxins removal (WHO, 2015).

A more detailed comparison among the performance of the treatment processes for the removal of cyanobacterial cells, intra- and extracellular cyanotoxins is reported in WHO (2015), as listed in Table 3.

3. Case study: lab-scale tests on conventional processes for cyanobacterial cells removal

The case study presented in this paper concerns some experimental tests carried out at lab-scale in order to optimize the functionality of conventional treatment processes applied in a full-scale drinking water treatment plant. Many utilities apply conventional treatments in their plants and the presence of a new pollutant often requires the optimization of conventional treatments already present in the plant rather than the use of advanced technologies and new plants. In particular, the tests, such as those described in this case study, are a useful support for assessing the performance of the treatment processes, already existing or of future implementation for upgrading a drinking water treatment plant. Therefore, these tests can guide the water company in choosing the best solutions to ensure a good performance in removing specific pollutants.

In this case study, experimental tests were performed in order to evaluate the efficiency of cyanobacterial cells removal with the following conventional treatments: micro screen, coagulation/flocculation, flotation, sand filtration, granular activated carbon (GAC) filtration and chlorine oxidation.

Table 2. Treatment performance for cyanobacterial cells and cyanotoxins for which guideline values have been established (WHO, 2015)

	Chlorination	***Ozonation***	***Coagulation***	***Activated carbon***	***Advanced oxidation***	***Membranes***	***Biological treatment***
Cyanobacterial cells			+++			+++	
Cyanotoxins	+++	+++		+++	+++		+++

+++ = 80% or more removal.

Table 3. Treatment performance for cyanobacterial cells and cyanotoxins (WHO, 2015)

	Cyanobacterial cells, intracellular cyanotoxins, geosmin and 2-methylisoborneol	***Extracellular free cyanotoxins***	***Extracellular (free) geosmin and 2-methylisoborneol***
Coa~~u~~gulation/sedimentation	+	-	-
Riverbank and slow sand filtration	+	+	+
Membrane filtration	+	-[a]	-[a]
Dissolved air flotation	+	-	-
Activated carbon	-	+	+
Ozonation[b]	-	+	+
Chlorination (free chlorine)[c]	-	+	-
Chloramination and Chlorine dioxide	-	-	-
Pre-oxidation	-	-	-

+ = 80% or more removal; - = not so effective; [a]Depends on the size of membrane (nanofiltration is effective); [b]Ozonation may release cyanotoxins and is not effective for saxitoxins; [c]Chlorination may release cyanotoxins and is not effective for anatoxin-a

All the experiments were performed directly on the raw water; however, it should be considered that these are complementary processes and therefore need to be evaluated according to a logic that reflects their combination in the real treatment plant.

3.1. Raw water quality

Raw water characteristics show that the main critical parameters are the microbiological contaminants and algae as shown in Table 4. These data were analyzed once a month during 10 month-period, during which the lab-scale tests for water treatment were also performed.

Table 4. Raw water quality (average quality of 11 samples)

Parameter		***Value (min-max)***
pH	pH unit	7.8-8.3
Color	mg/L Pt/Co	<1
Odor	-	<1
Turbidity	NTU	<1
Temperature	°C	10.8-12.7
TOC	mg/L	<1
Ammonia	mgNH_4^+/L	<0.05
Nitrate	mgNO_3^-/L	<2
Nitrite	mgNO_2^-/L	<0.03
Total colony count 22°C	CFU/1 mL	144->300
Total colony count 36 °C	CFU/1 mL	86- >300
Coliforms 37 °C	CFU/100 mL	<1-40
Escherichia coli	CFU/100 mL	<1-40
Enterococci	CFU/100 mL	<1-9
Clostridium perfringens	CFU/100 mL	<1-7
Algae	N/100 mL	230-1,800

3.2. Coagulation/flocculation

Several series of jar tests have been carried out (Fig. 1) in order to identify yields, operating conditions and characteristics of the sludge produced through the use of different coagulants ($FeCl_3$, PAC and $Al_2(SO_3)_4$) and flocculants for the removal of cyanobacteria by means of coagulation/flocculation/sedimentation.

Fig. 1. Jar test apparatus

It emerged that the aluminum sulphate has been excluded because, while showing a good efficiency in algal removal (50% -100%), it shows considerable difficulties in flocculation and sedimentation of the produced flakes. Ferric chloride presents the advantage of forming more stable flakes and producing less sludge than the PAC (15-40 mg/L SST of $FeCl_3$ versus 40-140 mg/L for PAC); the advantage of removing toxic algae in a variable percentage up to 100% and releasing high Fe residues in the supernatant.

The aluminum polychloride (PAC) proved to be the most effective (Fig. 2) both from the point of view of the removal of the algal load (with yields of 100%) and of the characteristics of sedimentation of the sludge and of the metal residue in the supernatant.

The only weak point is the high production of sludge, especially in view of a filtration by subsequent contact. The high-negatively charged organic polyelectrolyte is the only flocculant that is able to improve the yield of ferric chloride and to decrease its metal residues in the supernatant.

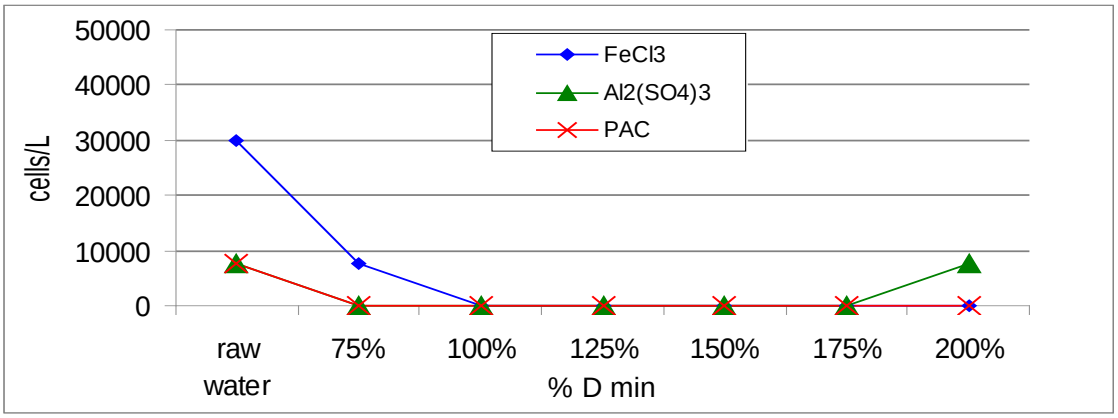

Fig. 2. Cyanobacteria cells concentration versus coagulant dose (indicated as percentage of the minimum dose) in the jar tests

3.3. Rapid multimedia filtration

Rapid multilayer filtration (sand/anthracite) shows that the simple filtration, in conditions of low algal load, proves sufficient for the total removal of algal content and for a good removal of suspended solids (22-92%). Although, in conditions of high algal load, reaches algae removal of 99.6%, however, reveals the need to be combined with other treatments for better control of cyanobacteria. The contact filtration shows a total removal of algae with both ferric chloride and aluminum polychloride. Filtration is more effective in removing ferric chloride residues rather than those of aluminum polychloride, in fact in the first case the Fe remains < 5μg/L as the value in the raw water, while in the second case the Al increases up to 27 μg/L.

3.4. Activated carbon

Filtration on activated carbon can be a good support for simple filtration in case of high algal content, in fact it offers a yield reduction of algal cells of 99.5%. It represents the best way to remove the toxins most frequently produced by cyanobacteria present in the lake (*Planktothrix* and *Microcystis*).

3.5. Disinfection with sodium hypochlorite

Disinfection with sodium hypochlorite has no effect on algal killing in high cell load conditions. The tested assays did not result in the formation of by-products such as trihalomethanes (THMs) in significant concentrations. In particular, at the chlorine concentrations applied (0.5-1.5 mg/L), the increased presence of algae did not show any increase in the formation of THMs as shown in Table 5.

3.6. Combined treatments

The results (Table 6) show that flotation alone can remove *Planktothrix* (*Oscillatoria*), that was the only cyanobacteria species detected in these tests, with an efficiency of about 90% (test FL1). This result can be improved if the flotation process is combined with a coagulation or polyelectrolyte and no differences were observed between the use of a coagulant (iron chloride or PAC; tests FL2 and FL3) or a polyelectrolyte (test FL4).

Better results were obtained with the addition of both a coagulant and a polyelectrolyte (FL5-6) followed by flotation.

The micro screen alone is an effective process for algae removal (test M1) but its efficiency can be significantly improved if it is followed by coagulation/flocculation and flotation (tests M2-3), where the yield improves up to 99.4%. The use of a sedimentation process after micro screen and coagulation/flocculation (test S1-2) instead of flotation (tests M2-3) decreases the total yield from more than 99% to 93%.

4. Conclusions

The experimental tests show that coagulation/flocculation was very efficient for algae removal. When this process was followed by DAF instead of sedimentation better results were obtained.

Table 5. Algae removal and trihalomethanes formation during the oxidation with sodium hypochlorite

Parameter	***Raw lake water***				***Lake water after storage***			
	Chlorine concentration ($mgCl_2/L$)				***Chlorine concentration ($mgCl_2/L$)***			
	0	***0.5***	***1***	***1.5***	***0***	***0.5***	***1***	***1.5***
Algae (cells/L)	375,000	255,000	240,000	230,000	1,500,000	1,500,000	1,350,000	1,575,000
Chlorophyll-a (mg/L)	1.5	1.2	1.2	1.5	10.4	10.8	2.3	8.6
Trihalomethanes (mg/L)	<5	<5	<5	<5	<5	<5	<5	<5

Table 6. Concentration and yield of *Planktothrix* removal with the combination of different processes

Sample	***Algae concentration (cells/L)***	***Yield of algae removal (%)***
RW	4,309,800	-
FL1	420,100	90,2
FL2	342,400	92.1
FL3	300,500	93.0
FL4	375,600	91.3
FL5	120,300	97.2
FL6	49,800	98.8
M1	218,000	94.9
M2	29,000	99.3
M3	27,000	99.4
S1	141,100	96.7
S2	286,400	93.4

RW = raw water; FL1: flotation; FL2: coagulation (iron chloride)+flotation; FL3: coagulation (PAC)+flotation; FL4: polyelectrolyte+flotation; FL5: coagulation (iron chloride)+polyelectrolyte+flotation; FL6: coagulation (PAC)+polyelectrolyte+flotation; M1: micro screen; M2: micro screen+coagulation (iron chloride)+flotation; M3: micro screen+coagulation (PAC)+flotation; S1: micro screen+coagulation (iron chloride)+sedimentation; M3: micro screen+coagulation (PAC)+sedimentation.

When the suspended solid flocs were removed by means of a flotation process the results were not influenced by the coagulant type (iron chloride and PAC) while better results were obtained with the addition of a polyelectrolyte. Otherwise, when the coagulation/flocculation was followed by a sedimentation process, iron chloride was better as it produced more stable flocs, a more easily settleable sludge and a lower sludge amount than PAC.

The sand filtration further improved the removal of cyanobacterial cells after their aggregation in the flocculation process. The micro screen could be applied as water pre-treatment as it could offer significant algae removal. The use of sodium hypochlorite for algae inactivation did not show promising results and the algae content did not seem to influence THMs formation.

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References

Acero J.L., Rodriguez E., Meriluoto J., (2005), Kinetics of reactions between chlorine and the cyanobacterial toxins microcysitins, *Water Research*, **39**, 1628-1638.

Bauer M.J., Bayley R., Chipps M.J., Eades A., Scriven R.J., (1998), Enhanced rapid gravity filtration and dissolved air flottation for pre-treattment of river Thames reservoir water, *Water Science and Technology*, **37**, 2.

Bernezeau F., (1994), Can microcystins enter drinking water distribution systems, *Toxic Cyanobacteria, Current Status of Research and Management*, Proc. of an Int. Workshop, Adelaide, Australia, 115-118.

Bernhardt H., Clasen, J., (1991), Flocculation of micro-organisms, *Journal of Water Supply: Research and Technology - AQUA*, **40**, 76-87.

Campinas M., Rosa M.J., (2010), Evaluation of cyanobacterial cells removal and lysis by ultrafiltration, *Separation and Purification Technology*, **70**, 345–353.

Chow C.W.K., Panglisch S., House J., Drikas M., Burch M.D., Gimbel R., (1997), A study of membrane filtration for the removal of cyanobacterial cells, *Journal of Water Supply: Research and Technology - AQUA*, **46**, 324-334.

Cook D., Newcombe G., (2008), Comparison and modelling of the adsorption of two microcystin analogous onto powdered activated carbon, *Environmental Toxicology*, **29**, 525-534.

Craig K., Bailey D., (1995), *Cyanobacterial Toxin Microcystin-Lr Removal using Activated Carbon. Hunter Water Corporation Experience*, Proc. 16th Federal AWWA Convention, Sydney, 579-586.

Croll B., Hart J., (1996), *Algal Toxins Customers*, Proc. UKWIR-AWWARF Technology Transfer Conference, Philadelphia.

Dixon M.B., Richard Y., Ho L., Chow C.W.K., O'Neill B.K., Newcombe G., (2011), A coagulation-powdered activated carbon-ultrafiltration — multiple barrier approach for removing toxins from two Australian cyanobacterial blooms, *Journal of Hazardous Materials*, **186**, 1553–1559.

Drikas M., (1994), *Removal of Cyanobacterial Toxins by Water Treatment Processes*, Proc. of Toxic cyanobacteria - A global perspective, Adelaide, 30-44.

Edzwald J.K., (1993), Coagulation in drinking water treatment: particles, organics and coagulants, *Water Science and Technology*, **27**, 21-35

Funari E., Scardala S., Testai E., (2006), *Potentially toxic cyanobacteria: ecological, and methodological aspects and risk assessment - ISTISAN Report 08/6*, National Institute of Health, Rome, Italy, On line at: http://old.iss.it/binary/publ/cont/08-6%20web.1208243077.pdf.

Funari E., Scardala S., Testai E. (2014), *Cyanobacteria: guidelines for managing blooms in bathing waters - ISTISAN Report 14/20* (in Italian), National Institute of Health, Rome, Italy, On line at: http://old.iss.it/binary/publ/cont/14_20_web.pdf.

Gajdek P., Bober B., Mej E., Bialczyk J., (2004), Sensitised decomposition of microcystin-LR using UV radiation, *Journal of Photochemistry and Photobiology* B*: Biology*, **76**, 103-106.

Gibbs R.J., (1983), Effects of natural organic coating on the coagulation of particles, *Environmental Science and Technology*, **17**, 237–240.

Gijsbertsen-Abrahamse A.J., Schmidt W., Chorus I., Heijman S.G.J., (2006), Removal of cyanotoxins by ultrafiltration and nanofiltration, *Journal of Membrane Science*, **276**, 252–259.

Hargesheimer E.E., Watson S.B., (1996), Drinking water treatment options for taste and odor control, *Water Research*, **30**, 1423-1430.

Health Canada, (2002), Guidelines for Canadian Drinking Water Quality: Supporting Documentation, Cyanobacterial Toxins – Microcystin-LR, On line at: http://hc-sc.gc.ca/ewh-semt/alt_formats/hecs-sesc/pdf/pubs/water-eau/cyanobacterial_toxins/cyanobacterial_toxins-eng.pdf.

Henderson R., Parsons S.A., Jefferson B., (2008). The impact of algal properties and pre-oxidation on solid-liquid separation of algae, *Water Research*, **42**, 1827-1845.

Hoeger S.J., Shaw G., Hitzfeld B.C., Dietrich D.R., (2004), Occurrence and elimination of cyanobacterial toxins in two Australian drinking water treatment plants, *Toxicon*, **43**, 639–649.

Huang W.-J., Cheng B.-L., Cheng Y.-L., (2007), Adsorption of microcystin-LR by three types of activated carbon, *Journal of Hazardous Materials*, **141**, 115–122.

Kull T.P., Backlund P.H., Karlsson K.M., Meriluoto J.A., (2004), Oxidation of the cyanobacterial hepatotoxin microcystin-LR by chlorine dioxide: reaction kinetics, characterization, and toxicity of reaction products, *Environmental Science and Technology*, **38**, 6025-6031.

Kull T.P., Sjövall O.T., Tammenkoski M.K., Backlund P.H., Meriluoto J.A., (2006), Oxidation of the cyanobacterial hepatotoxin microcystin-LR by chlorine dioxide: influence of natural organic matter, *Environmental Science and Technology*, **40**, 1504-1510.

Lam A., Prepas E., Spink D., Hrudey S.E., (1995), Control of hepatotoxic phytoplankton blooms; implications for human health, *Water Research*, **29**, 1845-1854.

Lambert T.W., Holmes C.F.B., Hrudey S.E., (1996), Adsorption of microcystin-LR by activated carbon and

removal in full scale water treatment, *Water Research*, **30**, 1411-1422.

Li L., Gao N-y., Deng Y., Yao J.-j., Zhang K.-j., Li H.-j., Yin D.-d., Ou H.-s., Guo J.-w., *(*2009*)*, Experimental and model comparisons of H_2O_2 assisted UV photodegradation of Microcystin-LR in simulated drinking water, *Journal of Zhejiang University SCIENCE A*, **10**, 1660-1669.

Mattei D., Melchiorre S., Messineo V., Bruno M., (2005), Toxic algal blooms in Italy: risk assessment and epidemiology - *ISTISAN Report 05/29*, National Institute of Health, Rome, Italy, On line at: http://old.iss.it/binary/publ2/cont/05-29.1140181875.pdf.

Merel S., Clement M., Thomas O., (2010) State of the art on cyanotoxins in water and their behaviour towards chlorine, *Toxicon*, **55**, 677-691.

Montiel A., Weltè B., (1998), Preozonation couplet with flotation filtration: successedful removal of algae, *Water Science and Technology*, **37**, 65-73.

Pendleton P., Schumann R., Wong S.H., (2001), Microcystin-LR Adsorption by Activated Carbon, *Journal of Colloid and Interface Science*, **240**, 1–8.

Petrusevski B., Van Breemen A.N., Alaerts G.J., (1995), Optimisation of coagulation conditions for direct filtration of impounded surface water, *Journal of Water Supply: Research and Technology - AQUA*, **44**, 93-102.

Rodrìguez E., Onstadb F.D., Kull T.P.J., Metcalf J.S., Acero J.L., von Gunten U., (2007a), Oxidative elimination of cyanotoxins: Comparison of ozone, chlorine, chlorine dioxide and permanganate, *Water Research*, **41**, 3381–3393.

Rodrìguez E., Majado M.E., Meriluoto J., Acero J.L., (2007b), Oxidation of microcystins by permanganate: Reaction kinetics and implications for water treatment, *Water Research*, **41**, 102–110.

Rositano J., Nicholson B.C., (1994), *Water Treatment Techniques for Removal of Cyanobacterial Toxins from Water*, Australian Centre for Water Quality Research, Salisbury, Australia.

Rositano J., (1996), *The Destruction of Cyanobacterial Peptide Toxins by Oxidants used in Water Treatment*, Urban Water Research Association of Australia, Melbourne, Australia.

Sorlini S., Collivignarelli C., (2011), Microcystin-LR removal from drinking water supplies by chemical oxidation and activated carbon adsorption, *Journal of Water Supply: Research and Technology - AQUA*, **60**, 403-411.

Sorlini S., Gialdini F., Collivignarelli C., (2013), Removal of cyanobacterial cells and Microcystin-LR from drinking water using a hollow fiber microfiltration pilot plant, *Desalination*, **309**,106-112

Teixeira M.R., Rosa M.J., (2006), Neurotoxic and hepatotoxic cyanotoxins removal by nanofiltration, *Water Research*, **40**, 2837–2846.

Tsuji K., Nalto S., Naohlsa K., Watanabe M.F., Suzuki M., Harada K., (1994), Stability of microcystins from Cyanobacteria. Effect of light on decomposition and isomeration, *Environmental Science and Technology*, **28**, 173-177.

Tsuji K., Watanuki T., Kondo F., Watanabe M.F., Nakazawa H., Suzuki M., (1997), Stability of microcystins from Cyanobacteria. IV. Effect of chlorination on decomposition, *Toxicon*, **35**, 1033-1041.

Wang H., Lewis D., Newcombe G., Brookes J., Ho L., (2009), Separated adsorption and bacterial degradation of microcystins in GAC filtration, *International Journal of Environment and Waste Management*, **3**, 236-243.

WHO, (1999), Toxic Cyanobacteria in Water. A guide to their public health consequences, monitoring and management, World Health Organization, Geneva, Switzerland, On line at: http://apps.who.int/iris/bitstream/handle/10665/42827/0419239308_eng.pdf?sequence=1&isAllowed=y

WHO (2004), Guidelines for drinking water quality - Volume 1 - Reccomandations, World Health Organization, Geneva, Switzerland, On line at: http://who.int/water_sanitation_health/dwq/GDWQ2004web.pdf

WHO, (2006), Guidelines for drinking water quality - Volume 1 – Reccomandations: addendum, World Health Organization, Geneva, Switzerland, On line at: http://apps.who.int/iris/bitstream/handle/10665/43242/9241546743_eng.pdf?sequence=1

WHO, (2011), Guidelines for drinking water quality, World Health Organization, Geneva, Switzerland, On line at: http://apps.who.int/iris/bitstream/handle/10665/44584/9789241548151_eng.pdf?sequence=1

WHO, (2015), Management of cyanobacteria in drinking water supplies: Information for regulators and water suppliers. Technical Brief, World Health Organization, Geneva, Switzerland, On line at: http://apps.who.int/iris/bitstream/handle/10665/153970/WHO_FWC_WSH_15.03_eng.pdf?sequence=1